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ELECTRICAL CONDUCTIVITY AND INFRARED RADIOMETRY OF STEAM

by

Hugh R. Carlon

Research Division

April 1980

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND

Chemical Systems Laboratory

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20. ABSTRACT (Contd)

into the understanding of the vapor-liquid phase transition in water. The results are important in meteorology, weather and climatology, and they have military implications.

PREFACE

The work described in this report was authorized and supported by Chemical Systems Laboratory In-House Laboratory Independent Research (ILIR) program funds under project 1T161101A91A. This work was started in July 1977 and was completed in September 1978.

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ELECTRICAL CONDUCTIVITY AND INFRARED RADIOMETRY OF STEAM

INTRODUCTION:

For a long time it was believed that the infrared absorption spectrum of water "vapor" could be explained by interatomic vibrations or by other modes of individual water molecules ("monomers"). The monomer is shown schematically in Figure 1.

But recent studies sponsored by the Chemical Systems Laboratory In-House Laboratory Independent Research (ILIR) program have shown quite conclusively that this absorption, which is often referred to as the infrared "continuum" absorption of water vapor¹, cannot be adequately explained by the monomer. Rather, it is thought to be due to molecular aggregates or "clusters" of water molecules in the vapor phase. These results have been published in the open literature²⁻⁶ and in local reports.⁷⁻⁸

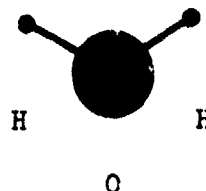


Figure 1. The Water Molecule or Monomer

Substances which absorb also emit infrared radiation. Thus the infrared emission spectra of water vapor, and especially of steam,⁴ show features which give clues as to water cluster species which are present. The infrared continuum absorption in the atmosphere presently is believed by many scientists to be a relatively minor absorber in spectral regions of high transparency, called "windows", through which infrared systems operate at wavelengths of 3-5 μ m, 8-13 μ m, and in other smaller window regions. However, new results including those discussed in this paper have shown that the continuum absorption depends upon complex cluster-forming mechanisms which are enhanced by ionic activity in the atmosphere and that the radiative transfer of the atmosphere, and hence the earth's climate, may be affected in ways that were not previously appreciated.

This ILIR effort, and most especially more recent work reported in this paper, have shown that if the infrared continuum absorption is due to water clusters and the mechanisms can be understood, it is possible that the atmospheric continuum absorption might be enhanced at will. If feasible, this enhancement would significantly affect field infrared systems performance. Other phenomena, such as nuclear blasts, may also greatly enhance the atmospheric continuum absorption for reasons which are only now becoming understood. Possible effects of nuclear radiation upon atmospheric infrared transmission are, quite obviously, of major interest. Since the continuum absorption in steam is hundreds to thousands of times stronger than in normal moist atmospheres, it was chosen as the medium for infrared and electrical measurements reported here.

MOLECULAR CLUSTERING IN WATER VAPOR:

Previous ILIR work²⁻⁸ has shown that the infrared continuum absorption is due to neutral water clusters which are present in enormous numbers in water vapor and have statistical distributions similar to that shown in Figure 2. In this figure, for saturated air ("s", the saturation ratio or fractional relative humidity, = 1.0) at 23°C, the estimated numbers per liter in moist air, $(N_N)_g$, of water clusters having "sizes" $(c)_N$ (numbers of monomers per cluster), are shown.

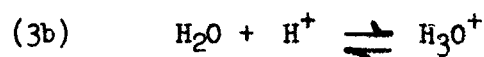
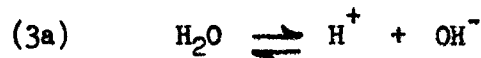
Although these clusters are electrically neutral, this work also showed many kinds of evidence that cluster populations are directly proportional to the numbers of hydrated ions which are present in water vapor under given conditions. The ion product of water is usually thought to be a property of bulk liquid water. Yet the results showed that the numbers of clusters which must be present to account for the infrared spectral behavior of water vapor ($s = 1.0$) were directly proportional to the ion product, which is highly temperature-dependent. The water cluster mass concentration in the vapor, C_c (g/m^3), always could be expressed as:

$$(1) \quad C_c = \frac{K s^2 p_o \sqrt{K_w}}{\theta_k}$$

where K is a proportionality constant, p_o is the vapor pressure of saturated water vapor, mm Hg, at temperature θ_k ($^{\circ}K$) and K_w is the ion product of water at that temperature. The ion product is density-independent, and can be closely related to temperature by an empirical expression⁹ which can be written:

$$(2) \quad K_w = \exp \left(\frac{-7156}{\theta_k} - 8.17 \right)$$

This evidence suggests that, at least in saturated water vapor at higher temperatures, for example, in saturated steam, the ions which form clusters might come from the dissociation of water itself:



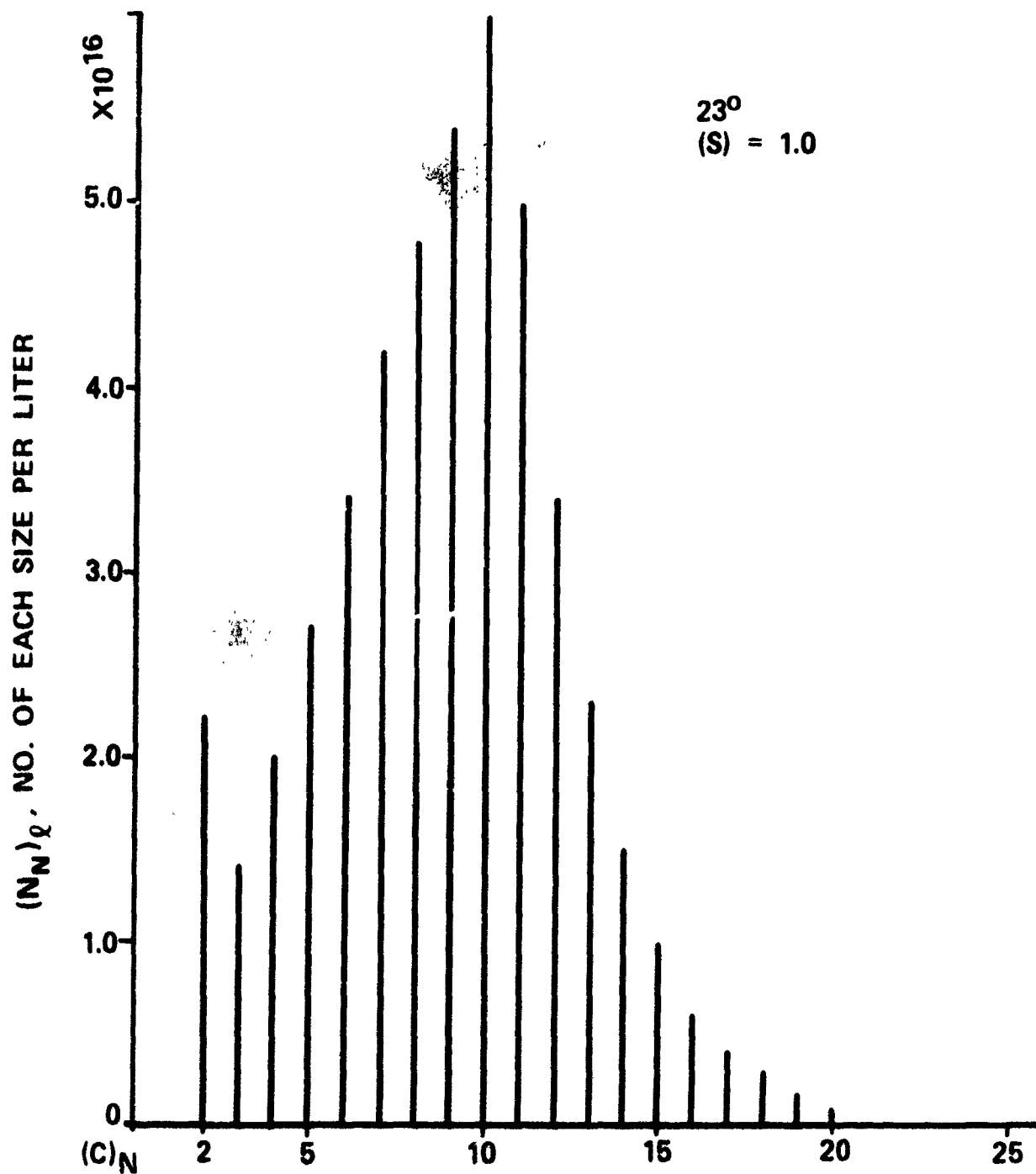


Figure 2. Cluster "Size" Distribution in Water Vapor or in Moist Air, 23°C, "s" = 1.0

Much is known about the spontaneous hydration of ions in water vapor, which occurs in less than a microsecond¹⁰ when a new ion is exposed to water vapor. The concept is shown by a simple model in Figure 3. Water molecules are shown as white spheres swarming or clustering about a central, positive or negative ion. This example shows 12 water molecules or monomers about the ion ("c" = 12).



Figure 3. Water Cluster Formed by Hydration of Ion ("c" = 12).

The concept can also be shown schematically, as in Figure 4, for the example of a positive or a negative ion clustered by four monomers ("c" = 4). Positive ions attract the oxygen atoms in the monomers, while negative ions attract the hydrogen atoms. Once the water monomers are clustered about the ions, they also begin immediately to "cross-link" with one another by hydrogen bonding. Thus, even when the ionic charge is lost an instant later, the clusters can remain together as hydrogen-bonded, neutral water clusters having peaked statistical distributions like that in Figure 2, for comparatively enormous periods of time. Experimental evidence shows that these clusters

can have lifetimes of from minutes to hours.

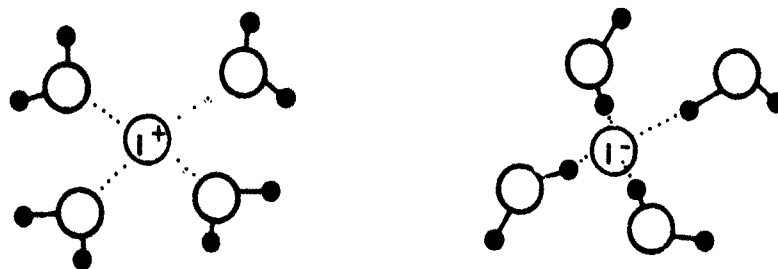


Figure 4. Examples of Positive and Negative Ion-Induced Water Clusters of "Size" Four Molecules ("c" = 4)

It is also well known that populations of ion hydrates such as those shown in the examples of Figures 3 and 4 have peaked statistical distributions where the mean cluster size, "c", is directly dependent upon the saturation ratio "s". Example distributions are shown in Figure 5 for ions formed by generating Pb^+ ions into water vapor at 300°K and at the "s" values and water vapor pressures shown in the figure.¹¹ In typical atmospheres, it is known¹² that the average ion hydrate or "water ion cluster" has a size of 10-12 monomers ("c" = 10-12). This is because each ionic charge has a lifetime measured in fractions of microseconds. Before charge neutralization, water monomers will be attracted to an ion in proportion to their numbers in water vapor, and these numbers will, of course, be proportional to the vapor pressure or to the saturation ratio, "s".

As the water monomers cluster about an ion and intermolecular hydrogen bonding begins, clusters are thus formed which can be stable even after the ionic charge is neutralized. Thus ion-induced, electrically neutral water clusters greatly outnumber the equilibrium ion populations at any instant, but they are proportional to them. These vast differences in ion and neutral cluster populations arise because of the comparatively enormous lifetimes of hydrogen-bonded neutral clusters vs. the ion charge lifetimes.

These interrelationships are shown in Figure 6, where the numbers of water monomers, clusters of size "c" = 10, and equilibrium ions are shown for saturated water vapor as functions of Celsius temperature, θ_c . The numbers of species are shown here for each cm^3 of vapor, compared to Figure 2 where each liter of vapor was considered.

In the author's infrared radiometric measurements of saturated steam⁴, intense spectral activity was observed which gave evidence for large water cluster populations and indicated that:

- 1.) A direct proportionality exists (as predicted by theory) between ion populations in water vapor or moist air,

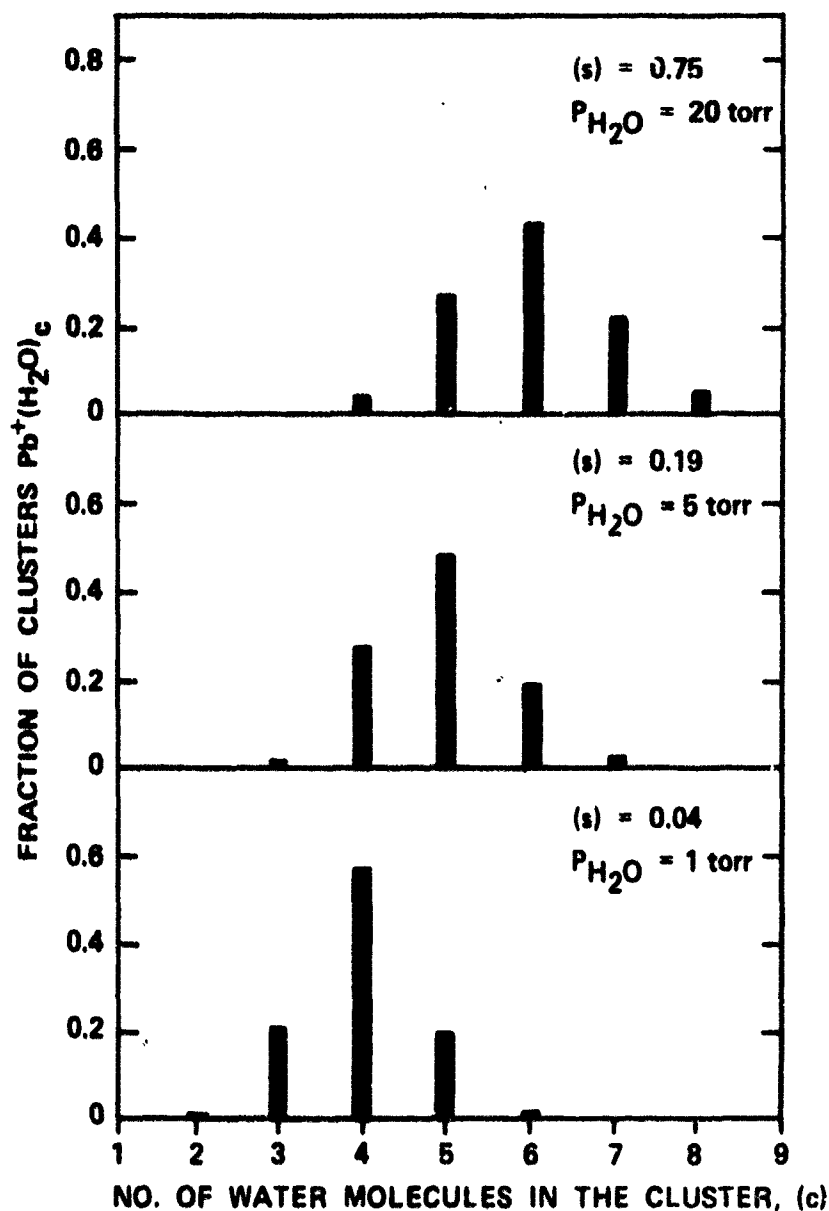


Figure 5. Distributions of $\text{Pb}^+(\text{H}_2\text{O})_c$ Ion Clusters at 300°K.¹¹

and infrared spectral activity; thus, it should be possible to measure electrical conductivity in water vapor which will have similar dependencies upon vapor pressure and temperature as these dependencies for infrared absorption and emission attributed to neutral water clusters;

- 2.) If steam were a rich source of infrared spectral activity attributable to clusters, it should be a rich source of hydrated ions for experimental work.

These observations led to the measurements described in the present paper.

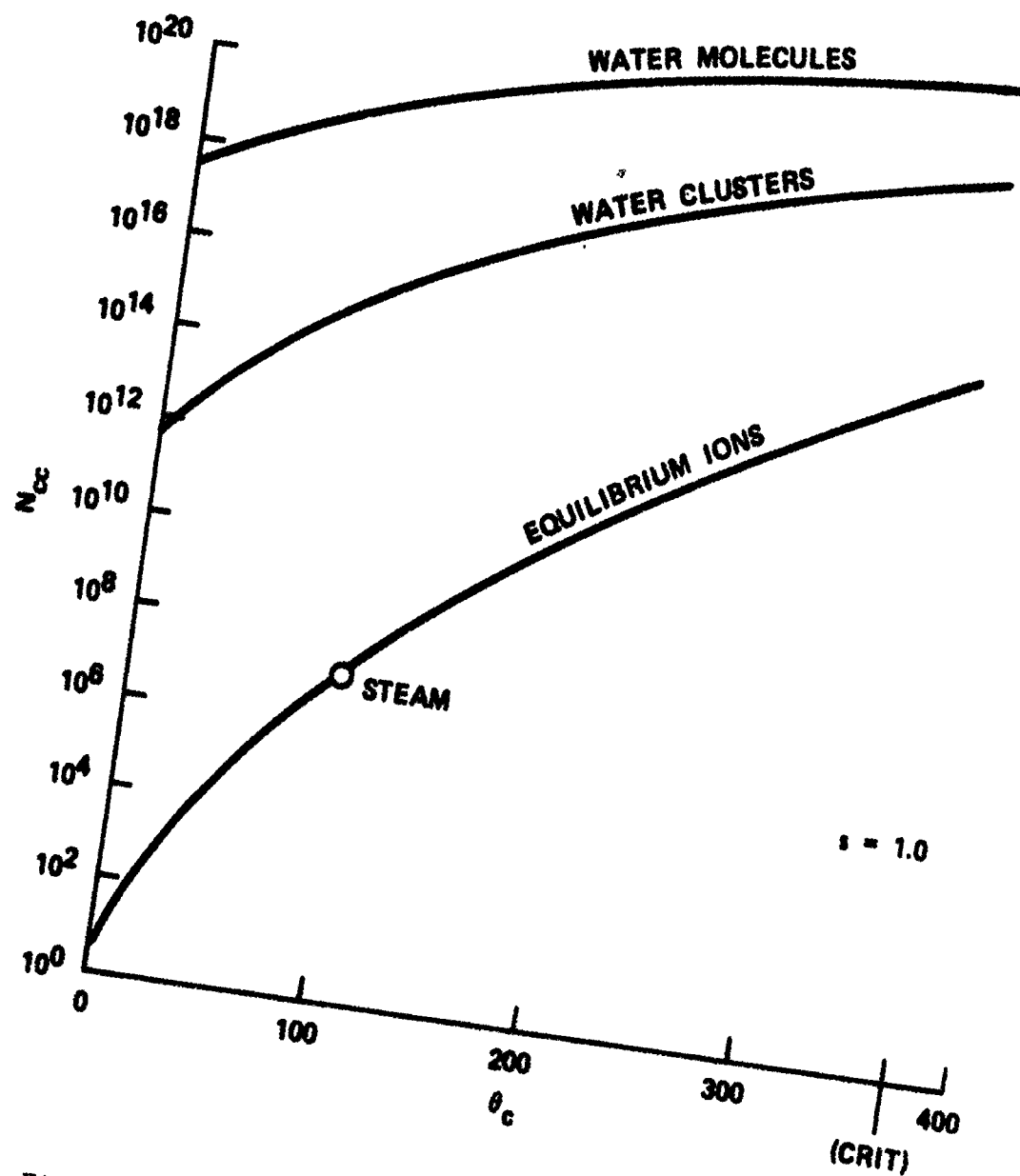


Figure 6. Numbers of Water Monomers, Clusters ($"c" = 10$) and Equilibrium Ions in Saturated Air or Vapor ($"s" = 1.0$) vs. Celsius Temperature.

EXPERIMENTAL SET-UP AND PROCEDURE:

The current density (j), amp/cm², for singly-charged ions in the vapor phase is:

$$(4) \quad j = N \, \eta \, \mu \, E,$$

where N is the number of ions per cm³, E is the electric field strength (volts/cm), η is the value of the electronic charge (1.6×10^{-19} coulomb) and μ is the ion mobility which for clusters of 10-12 water monomers ("c" = 10-12) is 1-2 cm²/volt-sec (Ref. 12). Thus for the direct current (DC) cells to be described below the electrical resistance or reciprocal conductance in megohms (R_m) is related to N by the expression:

$$(5) \quad N = \frac{L}{A} \cdot \frac{10^{-6}}{R_m \eta \mu}$$

where (L/A) is the "cell factor", or ratio of cell plate spacing to area (cm/cm² = cm⁻¹) which is the key design parameter for the vapor conductivity cell. Traditional devices for the measurement of the electrical conductivity of air, such as the Gerdien tube, have modest dimensions and poor cell factors. They rely on excellent insulators to carry the sampling electrodes, and they must be operated at low saturation ratios (relative humidities) to avoid electrical leakage between the electrodes which would enhance conductivity and give erroneous large ion counts.

A new kind of cell had to be designed for these measurements which could operate at temperatures up to 100°C and saturation humidity ("s" = 1.0), that is, under conditions of saturated steam. The dependency of cluster activity in water vapor and its proportionality to the ion product with temperature were known from the infrared measurements. Thus, it was possible to design a cell of adequate cell factor based upon the novel concept of an "ion product" in water vapor. The design calculations dictated that an $L/A = 10^{-5}$ cm⁻¹ would be required for marginal sensitivity using simple electronic instrumentation at normal room conditions, and that such a cell would give very good sensitivity for measurement of ion concentrations at higher temperatures and humidities.

The sample cell actually constructed had 40 parallel steel plates with an area (A) of 6.6×10^4 cm² spaced $L = 0.66$ cm apart. To compensate for electrical leakage across the insulators at higher humidities, a reference cell also was fabricated having an identical insulator configuration but a much smaller plate area (2600 cm²). Both cells are shown in Figure 7 and a close-up view of the reference cell, showing the insulator configuration common to both cells, is shown in Figure 8.

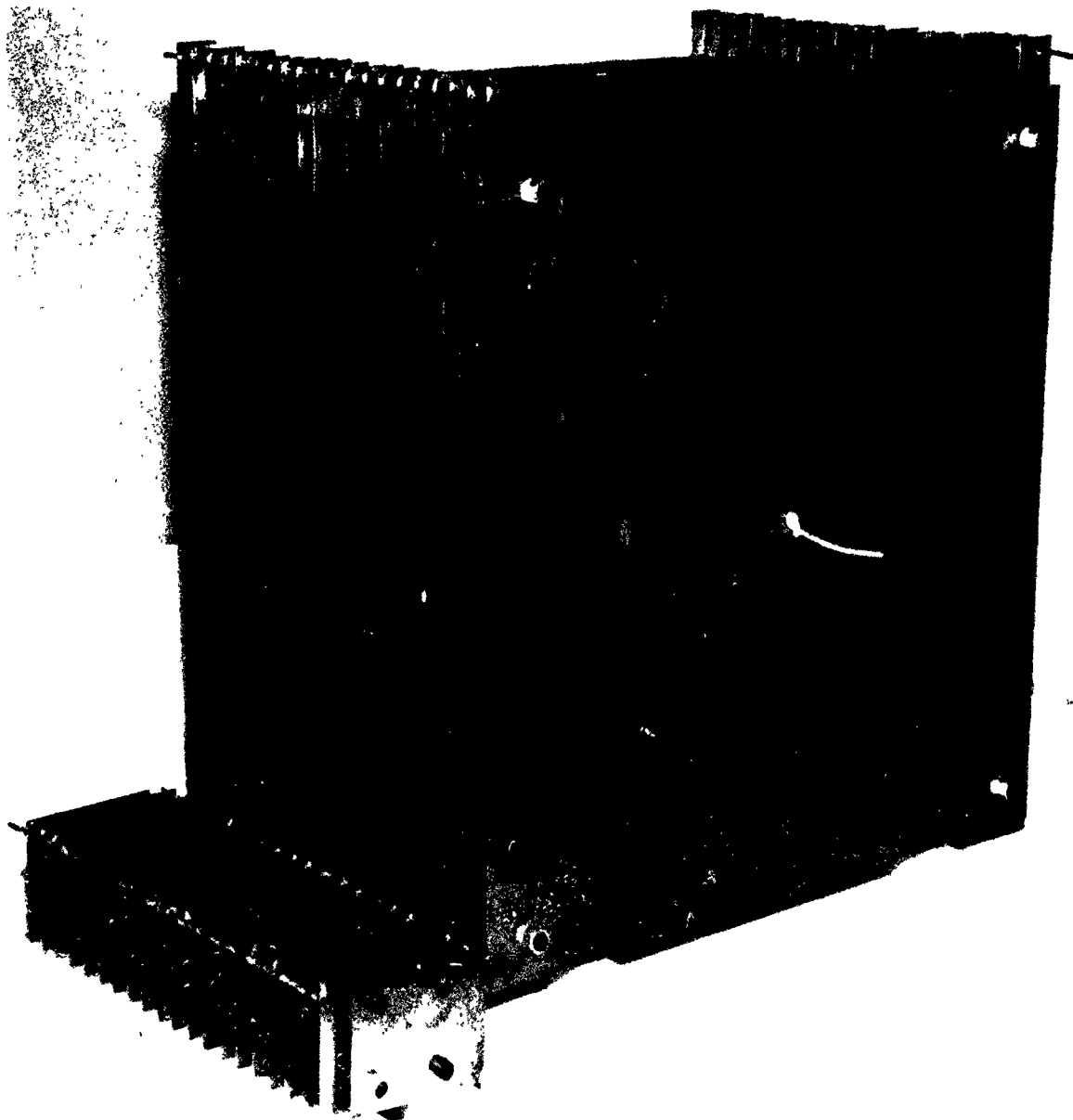


Figure 7. Electrical Conductivity Cells of New Design; the Large Sample Cell and Small Reference Cell Had Identical Insulator Configurations; For Scale, Cell Depth = 30cm.

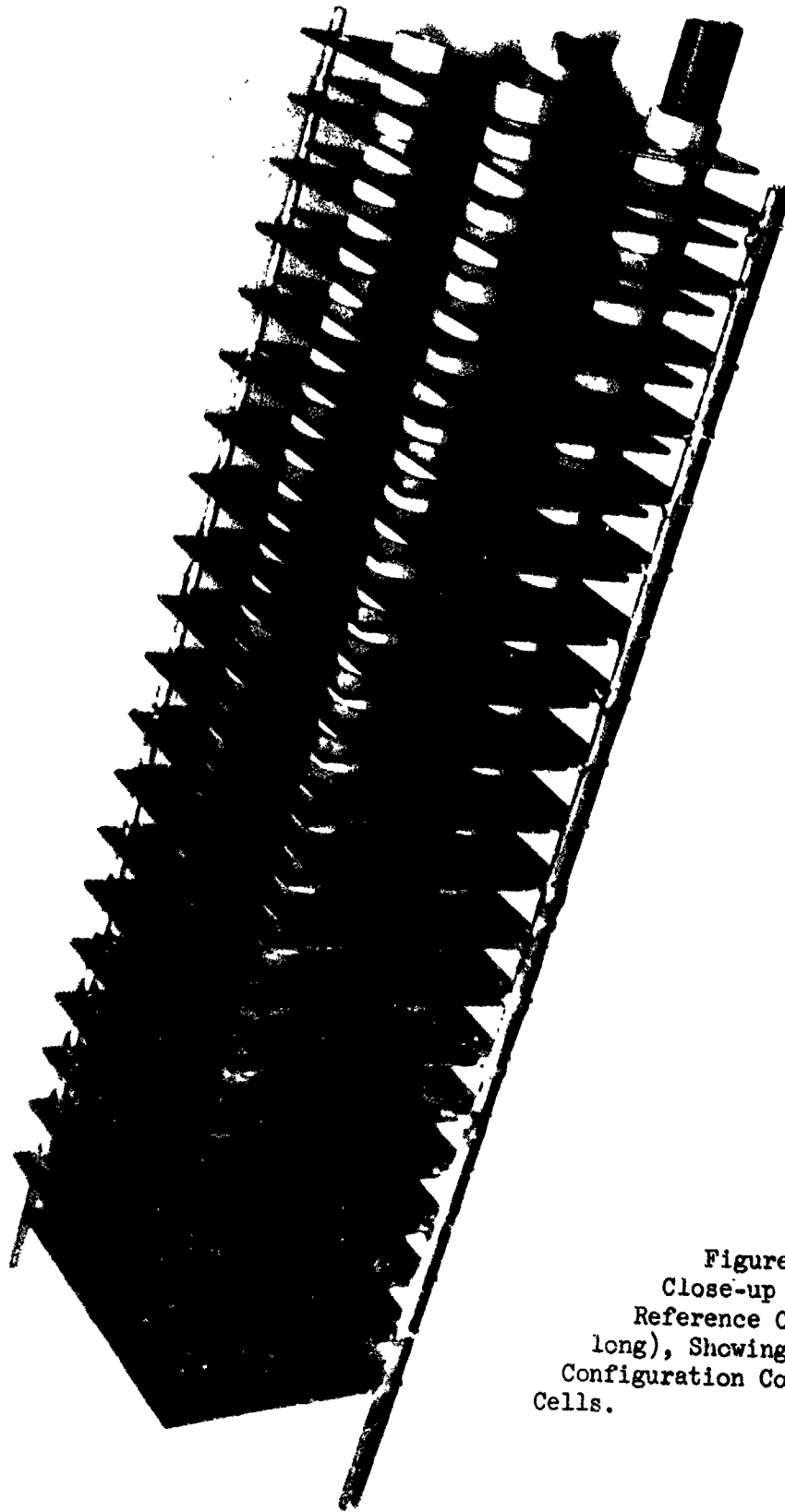


Figure 8.
Close-up View of
Reference Cell (30cm
long), Showing Insulator
Configuration Common to Both
Cells.

Insulator leakage also was studied in these measurements. By designing both cells optimally, and then dealing directly with residual leakage rather than by going to extraordinary lengths to avoid it, good experimental reproducibility was obtained.

The large sample cell consisted of 40 1-mm-thick steel plates, each 41 cm square (Figure 7). Alternating plates were connected to either of two bus wires running the length of the cell, somewhat in the fashion of the plates in an automotive storage battery but with moist air as the electrolyte in this case. Since L/A for the sample cell was $0.66/6.6 \times 10^4 = 10^{-5} \text{ cm}^{-1}$, from Equa. 5 for this cell:

$$(6) \quad N \approx \frac{3 \times 10^7}{R_m}$$

The plates in both cells were supported by five 8-mm-diameter resin-impregnated fibreglass rods with nylon spacers 0.66 cm thick. These materials were selected for their high electrical resistance, but were not the only materials tried. Teflon rods and spacers were used in other cells which were constructed during the two-year period over which these tests were carried out. However, the teflon insulators gave extremely troublesome surface effects, and they were abandoned in favor of the materials described above which gave reproducible results and negligible shunting resistances compared to those of typical moist air samples. Nevertheless, care was taken to minimize contact area between rods, spacers and steel plates. As a result, despite the very large dimensions of the cells, leakage resistances at ambient temperature and 50% relative humidity ("s" = 0.5) averaged 10^{10} to 10^{11} ohms.

The cell factors, L/A , of both cells were checked after cell fabrication by treating the cells as capacitors with air dielectrics and determining their electrical capacitances with an impedance bridge, from which:

$$(7) \quad \frac{L}{A} = \frac{8.85 \times 10^{-8}}{C_{uf}}$$

where C_{uf} is the capacitance in microfarads. Tests conducted over wide ranges of temperature and humidity confirmed that the electrical leakage characteristics of the insulators in both cells were nearly identical. In all experiments, both cells were always mounted and measured in the same way. Thus, differences between the sample and reference cell resistances in actual experiments could be attributed

solely to the conductivity of the moist air between the cell plates. In all experiments where water vapor condensation on the insulators was possible, the compensating cell was always placed in the most disadvantageous position within the test chamber- that is, the position where condensation, if it occurred at all, would affect the compensating cell insulators to a greater extent than the large (sample) cell insulators. In this manner, conductivities attributed to moist air were always conservative if, in fact, any condensation occurred.

Extensive testing was done with the compensating cell to study insulator leakage effects as functions of temperature and humidity. The most interesting observation was that insulator resistance plots had the same general shapes as moist air plots, except that the magnitudes of moist air conductances were about 10 to 30 times greater than those of the insulators. In other words, the data indicated that the same kinds of ionic species were present on the insulators as in the air, and were largely responsible for the insulator leakage. But except under high temperature and near-saturation humidity conditions, the ion populations on the insulators never approached those in the moist air between the plates of the sample cell.

Field strengths (E) of from 1 volt/cm to 100 volts/cm were used in the work reported here, after it was verified that Ohm's Law was obeyed, that is, that no additional ions were produced by the field. This was accomplished by exposing the cells to moist air at various temperatures and humidities for which cell resistance readings were taken as the cell voltage was increased. Three sets of test data are summarized in Figure 9. It can be seen that, within the limits of measurement error, there was no change in the sample cell resistance with changes in E , that is, the curves are flat. On this basis, a cell bias voltage of 20 volts was selected for general use.

Because of the large dimensions of the cells, it was found that electrometers or other extremely high-impedance devices were not required for sensitive measurements. In most cases, cell resistances could be determined easily by using a vacuum-tube voltmeter with an 11 megohm input impedance directly in series with the bias supply and the cell under test, and measuring voltage division as shown in Figure 10. For convenience, graphical solutions were worked out so that readings could be converted directly to cell resistances and then compared to theoretical values predicted from theory developed in the earlier ILIR work. A solution worksheet is shown in Figure 11.

The polarity of the bias voltage had little effect upon cell resistance. A small voltage was sometimes measured on the large, sample cell (about 0.02 volt) in the absence of bias. But this was negligible compared to voltages measured during normal operation. The 0.66 cm cell plate spacing was chosen to allow adequate circulation of moist air between the plates and to reduce the likelihood of short-circuiting. When the cells were placed in constant use, it was found that short circuits sometimes would occur due to "whiskers" of contamination which bridged a spacer between two plates. But without exception, the cell could be "cleaned" and restored to normal operation by the momentary application of a 400 volt bias directly across the plates.

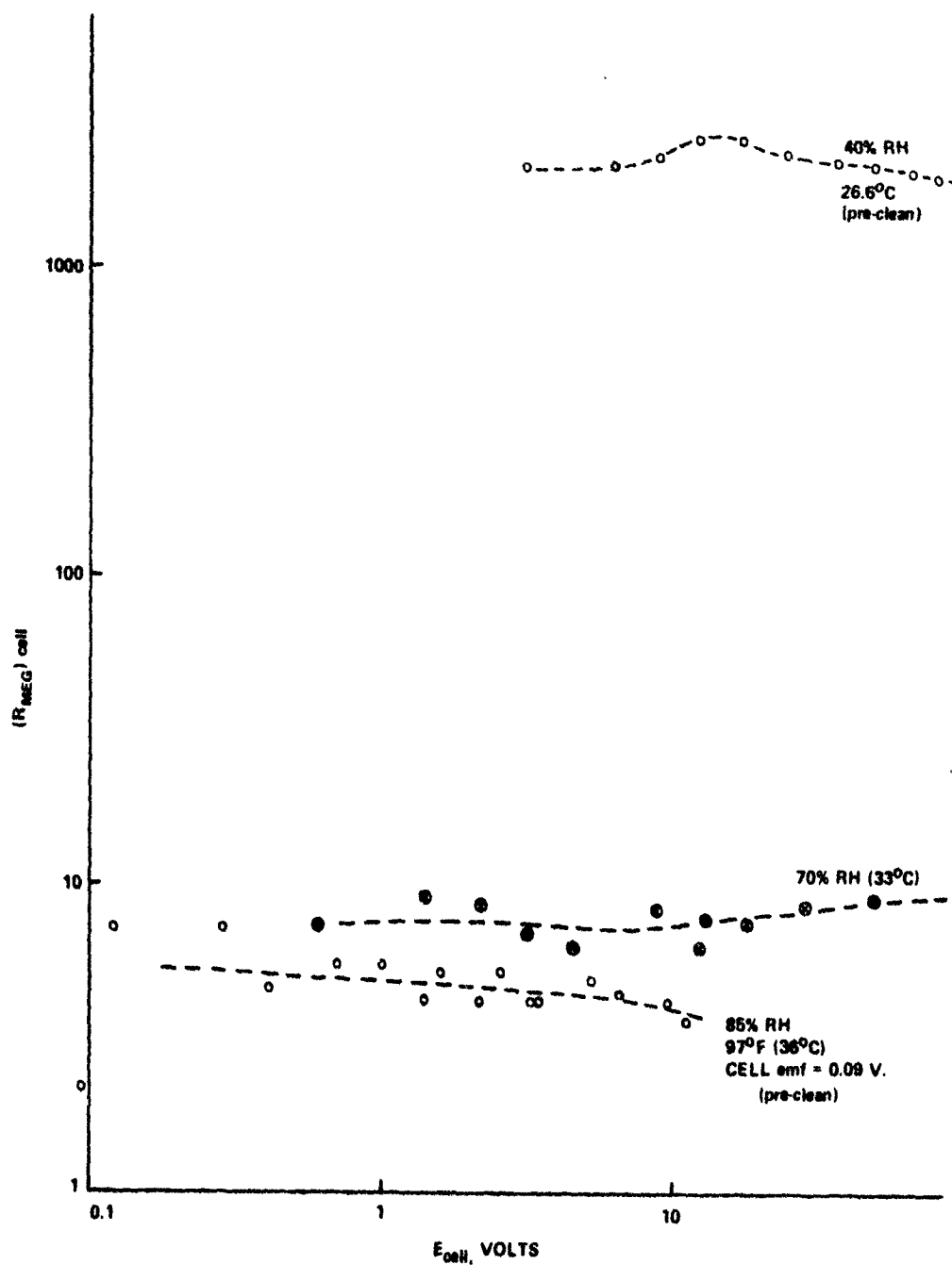


Figure 9. Effect of Bias Voltage upon Sample Cell Resistance for Three Different Temperatures and Humidities.

Therefore, this procedure was routinely adopted for use before experiments where unusual sensitivity was required.

Electrical conductivity tests were carried out in a steam test chamber or cabinet shown in two views in Figures 12 and 13. Only the large, sample cell is shown in the cabinet in these early photographs,

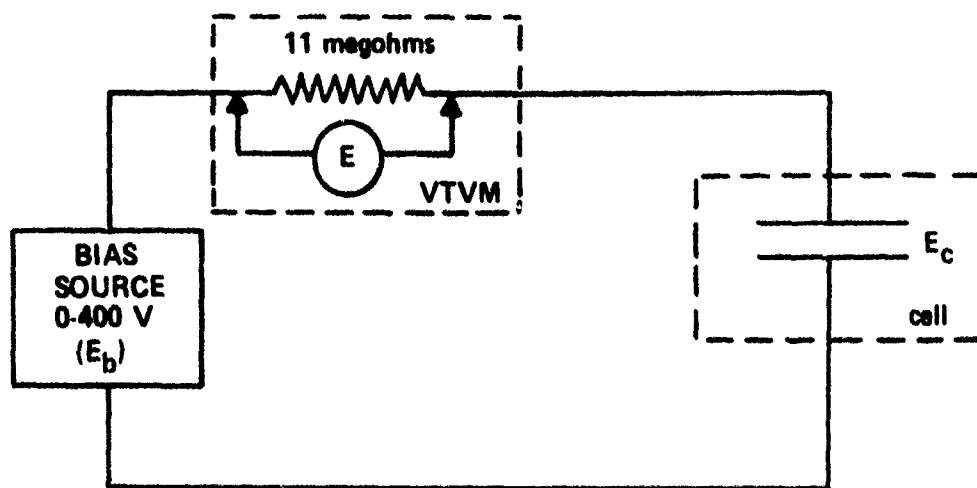


Figure 10. Technique of Measurement of Cell Resistance.

but the reference (small, compensating) cell was always placed closer to the point of steam introduction than was the large, sample cell during all experiments involving both cells, for reasons which have already been explained. All data reported in this paper were taken under steady-state conditions with DC fields and stagnant, moist air between the cell plates. These conditions were quite different from those normally used with the Gerdien tube, where the conductivity of a flowing gas stream is sampled with as little disturbance to the sampled volume as possible. However, these steady-state conditions were nearly identical to those established in earlier ILIR radiometric measurements of saturated steam and cooling, steam-generated water clouds⁴ which had provided the provocative results that suggested the present measurements.

Water was boiled at 100°C (atmospheric pressure) in the compartment seen on the right end of the test cabinet in Figures 12 and 13. The vapor generated by boiling was admitted through a slit into the large cabinet volume where the cells were located. The vapor passed first over the small cell and then over the large, sample cell. Resistances of both cells were constantly measured.

When sufficient water vapor had been generated and admitted to the large cabinet compartment, the slit was closed and the cell compartment was sealed at atmospheric pressure. Provisions were made to heat the air in the sample compartment with a small hotplate, and to vent the compartment quickly to room air when desired. Each moist air sample was allowed to equilibrate before readings were taken for retention. The amount of water vapor entering the sample compartment was sufficient to cause about a one degree increase in temperature during steam introduction, for example, from 26°C to 27°C in most trials.

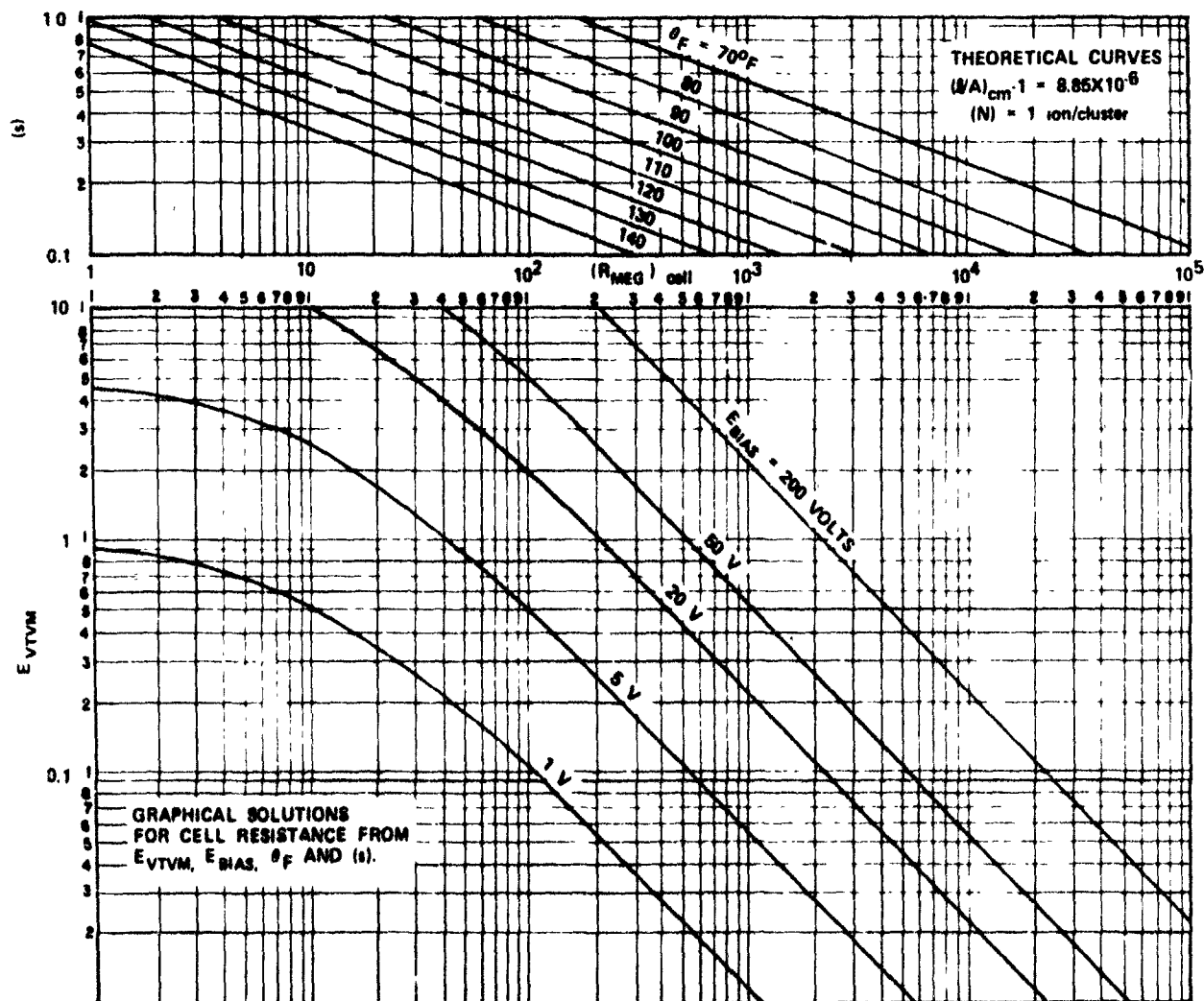


Figure 11. Graphical Solutions for Cell Resistances and Comparison With Theory.

RESULTS AND DISCUSSION:

Typical behavior of the resistance of the large, sample cell with humidification with water vapor generated by boiling is shown in Figure 14. The dashed curve indicates the reference (small, compensating) cell whose resistance is determined almost exclusively by insulator leakage. The solid curve represents the resistance measured for the moist air between the large, sample cell plates only. This curve is obtained by correcting the actual resistance of the sample cell for the leakage of the insulators measured for the reference cell with an identical insulator configuration. Thus, the dashed curve can be thought of as representing ions on the insulators, while the solid curve can be thought of as representing ions in the moist

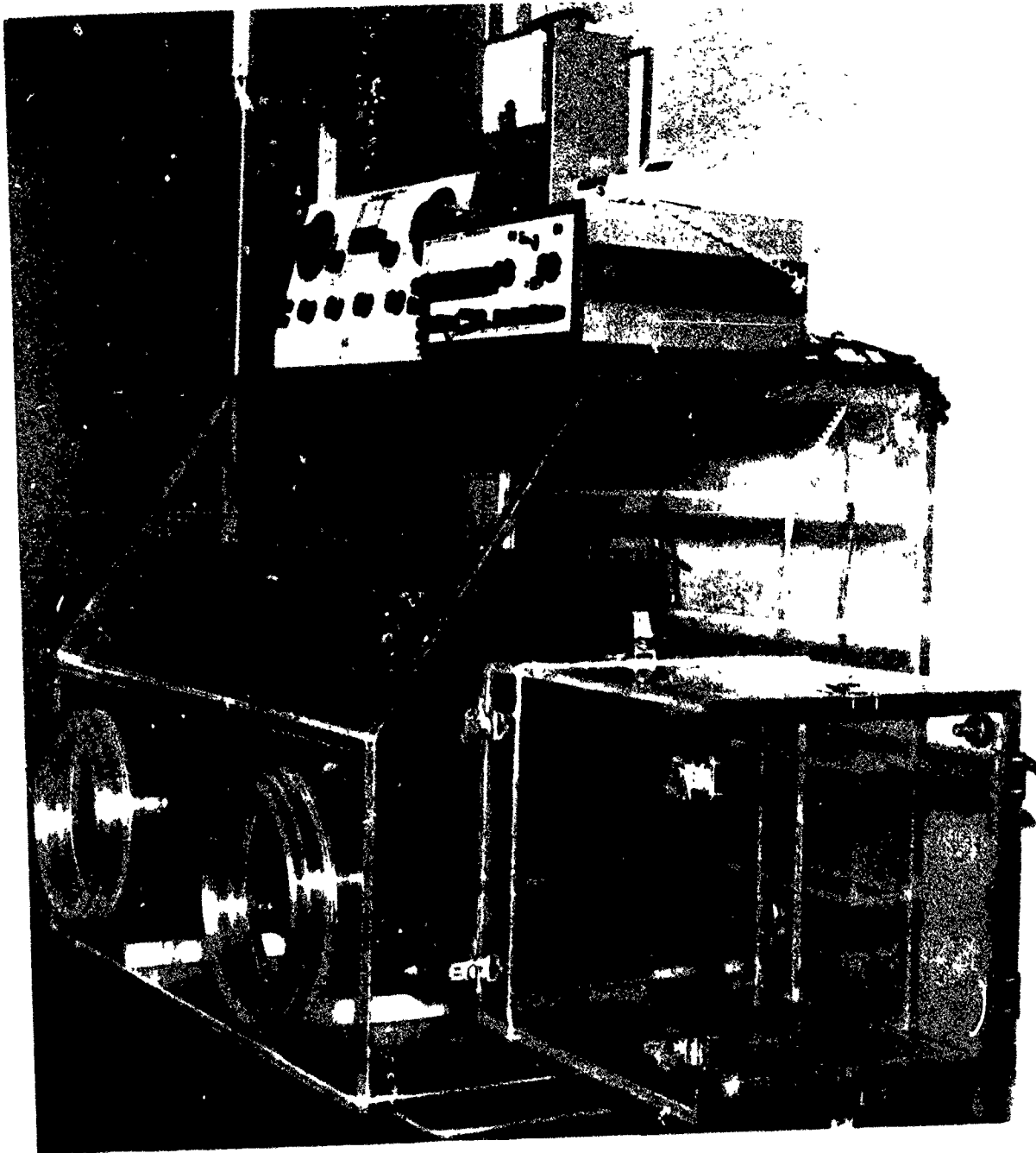


Figure 12. Electrical Conductivity Test Cabinet, End View.

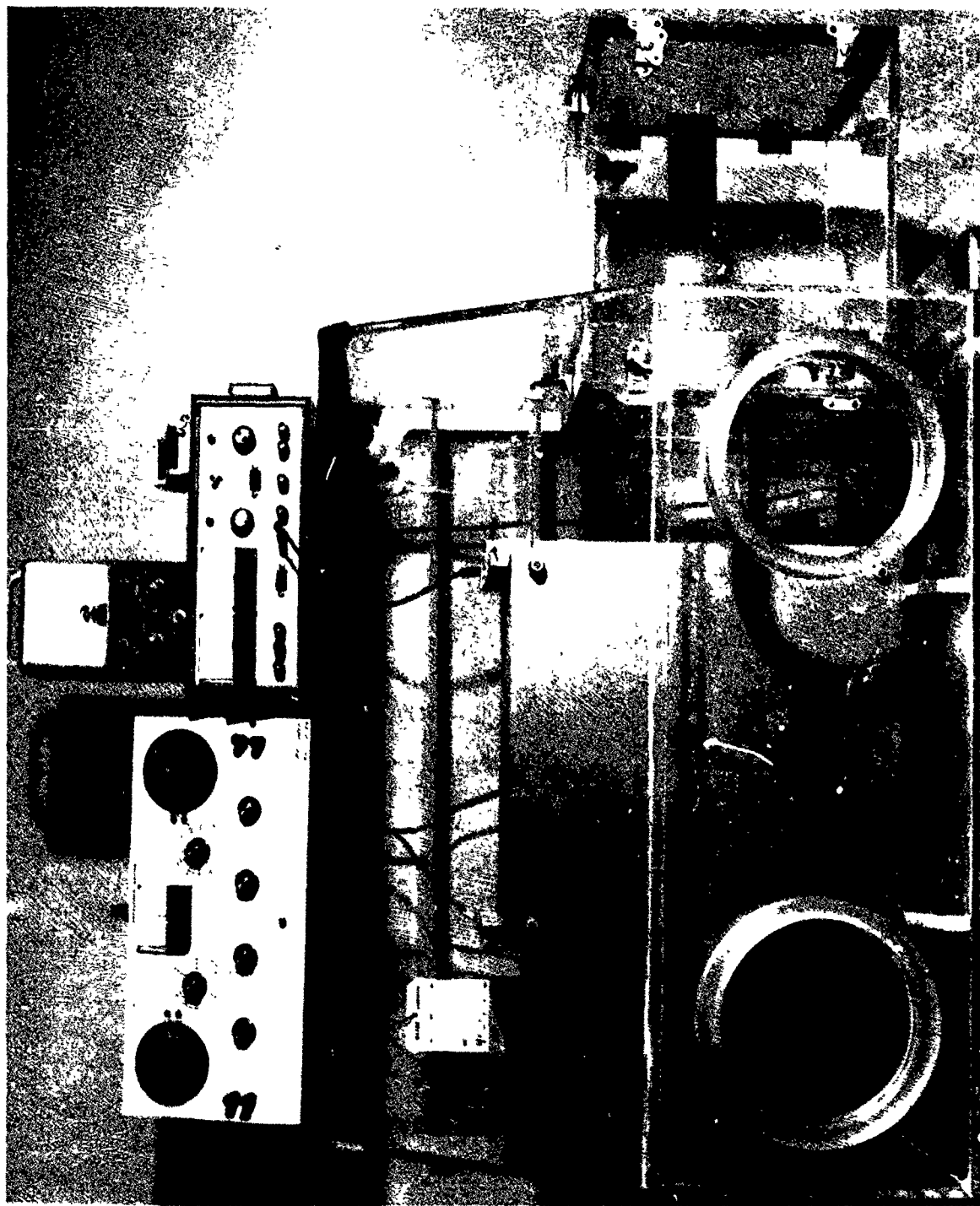


Figure 13. Electrical Conductivity Test Cabinet, Front View.

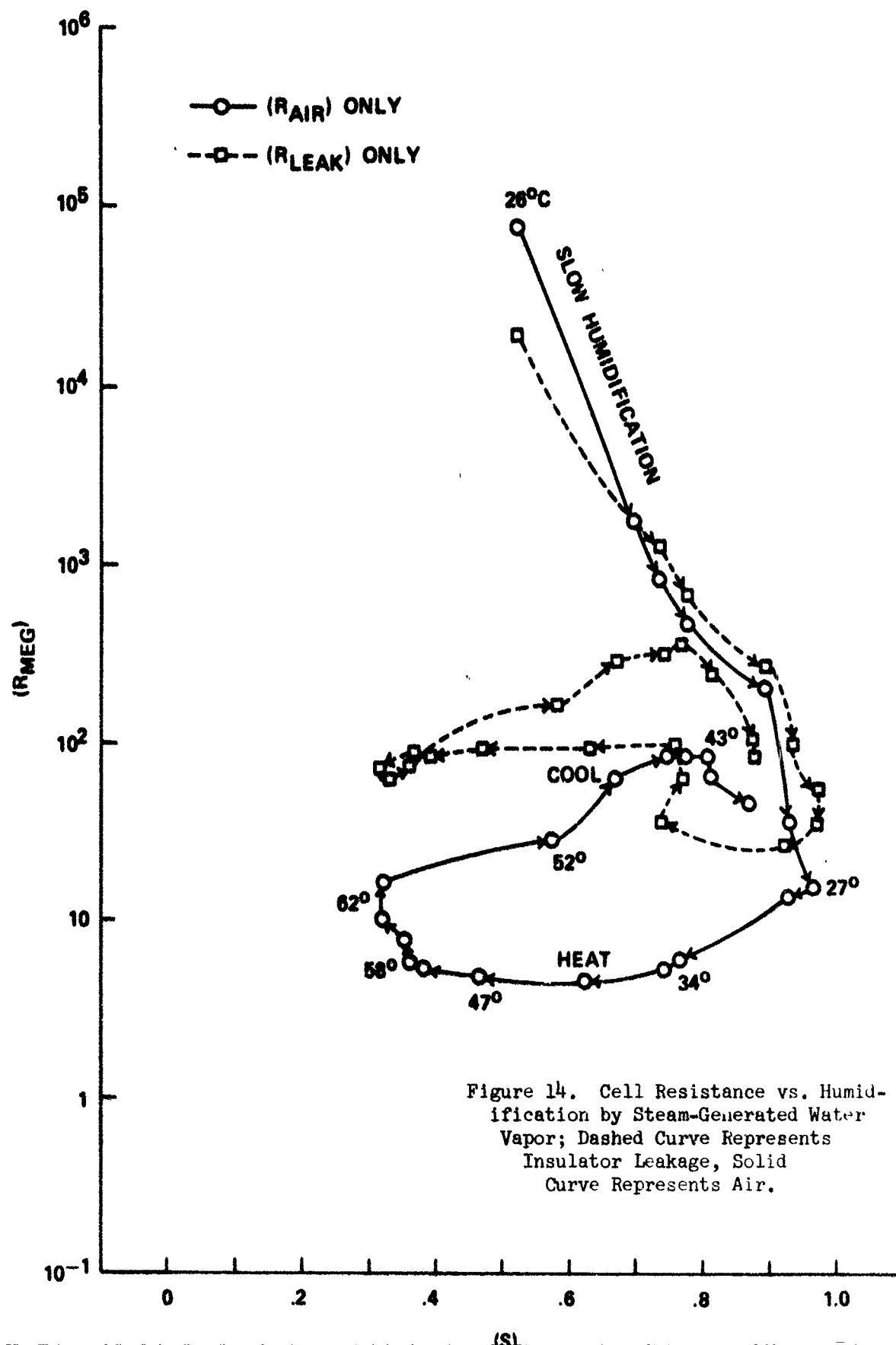


Figure 14. Cell Resistance vs. Humidification by Steam-Generated Water Vapor; Dashed Curve Represents Insulator Leakage, Solid Curve Represents Air.

air sample. At the beginning of these particular trials (upper ends of curves in Figure 14) the leakages of the insulators dictated the resistances of both cells (about 3×10^{10} ohms). But as slow steam humidification progressed, the "leakage" of the moist air rapidly overtook the insulator leakage as the major contributor to overall conductivity of the sample cell.

In these trials, after humidification when the steam sampling slit in the cabinet was closed to exclude further vapor, a hotplate was used to increase the temperature of the moist air sample in the compartment from 29°C to about 62°C . This decreased the saturation ratio "s", as shown on the abscissa of Figure 14, from a value near saturation to $s = 0.3$, but the measured resistances of both cells remained about the same indicating that the numbers of ions did not change appreciably.

The moist air sample was then allowed to cool, as shown by the upper parts of the "loops" in the curves of Figure 14. By the completion of the experiment, which in this case lasted for 3 hours and 39 minutes, the insulators had become sufficiently saturated with moisture to bring their resistance down to a level close to that of the residual moist air between the large, sample cell plates.

Another way to look at the data of Figure 14 is to convert the moist air resistance readings to ion concentrations by using Equation 6. The result is shown in Figure 15. At the beginning of the experiment, the test cabinet contained ambient air having about 300 ions per cm^3 and representative of expected values of 100-300 ions per cm^3 found in water vapor or in moist air under typical room air conditions. However, as the air was humidified by water vapor generated by boiling, the ion count increased very rapidly to levels of 10^6 - 10^7 ions per cm^3 . This ion concentration was maintained, and even slightly enhanced, as the moist air sample was heated.

Since these measurements were made in stagnant rather than in flowing air, the results imply that an ion regeneration mechanism maintained rather stable populations of ions for periods of up to an hour or more. Finally, when the sample compartment was vented to room air and the moist air sample was allowed to mix and cool, N began to return to normal. The peak value of N reached in this experiment (Figure 15) in which ions were generated by boiling water, namely, about 10^7 per cm^3 , is in agreement with this same value calculated for steam at 100°C on the curve labeled "equilibrium ions" in Figure 6.

The results reported here were obtained under conditions which differ from those of usual electrical conductivity measurements in at least two important respects: 1.) the air samples were allowed to equilibrate between the cell plates; they did not flow rapidly through the cell; 2.) a very sensitive cell was used, for which the insulator leakage as a contributor to measured resistance or conductance was accurately known under all conditions. Thus, the results cannot be compared directly to those of conventional measurements of atmospheric ion concentrations. They suggest that an incomplete understanding exists

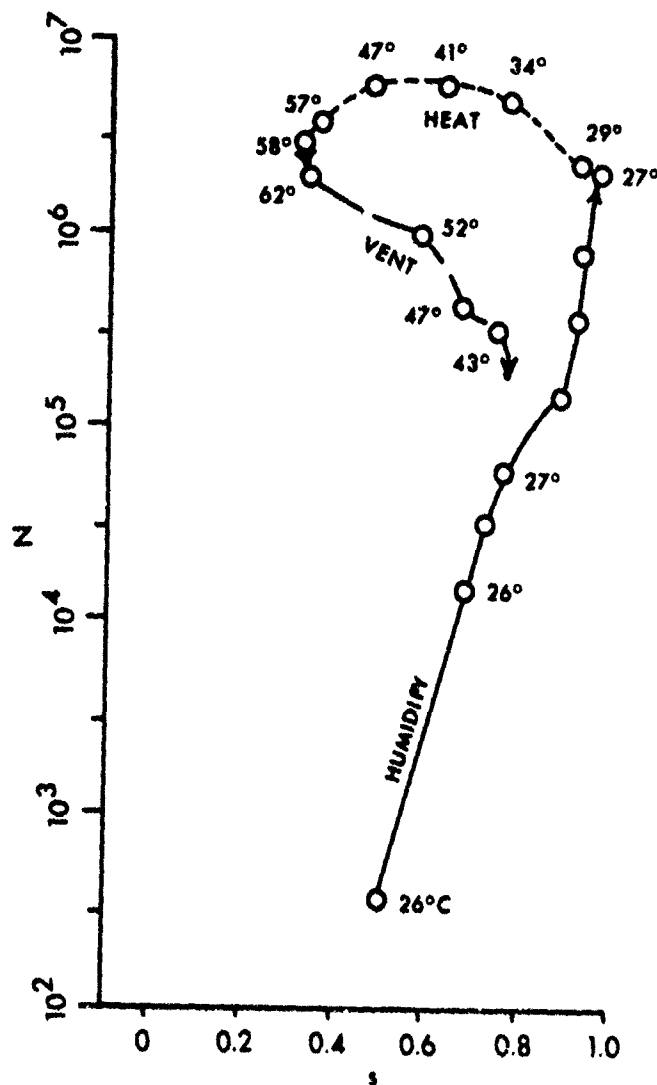


Figure 15. Number of Ions per cm^3 of Moist Air Humidified by Steam, vs. the Saturation Ratio, "s".

of the hydrated ions present in moist air, of their dependency upon the means by which they are generated, and of their role in inducing the formation of much larger populations of neutral water clusters in the vapor phase which can exhibit substantial infrared absorption and emission. Apparently, steam contains large numbers of ions which may be present simply because of the strong positive temperature dependence of water's ion product (Equation 2). The water cluster concentration necessary to explain the infrared continuum absorption already has been shown to be proportional to this same ion product (Equation 1).

If self-dissociation of water vapor were a significant source of ions (Equation 3) at, say, 27°C , this contribution at 100°C from Equation 2 would be about 100-fold larger in water vapor over boiling water

than in normal ambient, saturated air. But this would account for only two of the four orders of magnitude change shown in Figure 15. It is well known that newly-formed ions in water vapor are swarmed by water monomers and are hydrated in less than a microsecond¹⁰ as has already been discussed. Thus, the assumption that the species measured here are almost certainly small, singly-charged hydrated ions having mobilities of 1-2 cm²/volt-sec seems justified.^{12,14} Blanchard¹⁵ has shown that ions can be generated by bursting bubbles which are sure to be present at the surface of boiling water, but the magnitude of this effect is less than that necessary to explain the results under discussion in the present work. Possibly evaporation of tiny droplets torn loose from the surface also contributes to the ion concentrations. Together, these three effects might explain the observed initial ion concentrations.

The apparent regeneration of the ions measured by the author also raises questions, especially since the moist air samples were stagnant as the ions were continually being drawn to the cell plates as the cell currents were measured. These measurements were carried out in a normal laboratory environment. No high-powered electromagnetic sources or other unusual ion generation sources were present. When the moist air sample was vented to and mixed with room air, the ion count fell rapidly to normal laboratory levels. Ordinarily, results such as those observed here would suggest that electrode or insulator leakage had accounted for this behavior. But this seems extremely unlikely in view of the precautions taken, the techniques used, and the reproducibility observed in these measurements. Thus, the results suggest new findings which are not yet explained by theory.

The conductivity results, including those from the studies of insulator leakage, indicate that conductivity of moist air might be a more important factor than was previously realized in space charge dissipation. Presently, it is believed¹⁶ that insulator leakage effects rather than moist air conductivity can explain certain phenomena, for example, the well-known humidity dependence of annoying static-electric shocks received by persons moving and touching objects in dry, heated rooms in wintertime. In fact, some of the new data suggest that the electrical conductivity of moist air has a quadratic, or even a cubic, dependence upon its saturation ratio. One might also consider possible physiological effects due, for example, to high ion concentrations generated by boiling water room humidifiers.

CONCLUSIONS AND PLANS FOR FUTURE WORK:

These measurements of the electrical conductivity of steam and of moist air humidified by boiling water show that the ion content increases very rapidly with temperature of vapor generation and that the infrared absorption or emission which is observed can be accurately modeled as a function of the ion product of water with temperature. This allows the possibility that, at least at higher temperatures, hydrated ions or ion-induced, neutral water clusters which have infrared spectral activity can be generated by the dissociative ionization

of water, itself.

New ILIR funds have been made available for a continuation of these studies. The nature of water cluster species present in water vapor is dependent upon parameters not previously considered to be important, for example, the temperature at which water vapor is generated and the method of generation which is used. Such factors affect the kinds and numbers of infrared-active cluster species which are generated. Thus, carefully-designed experiments will have to be carried out in a multi-pass optical cell (shown in Figure 16) which is capable of providing optical paths of up to 200 meters on a mounting bed only 5 meters long. The cell will be provided with an adjustable electric clearing field so that the effect of ion removal from water vapor upon infrared continuum absorption in the 8-13 μ m wavelength region may be studied. Absorption spectra will be obtained for water vapor generated at a variety of temperatures and by using different methods of generation, and the conductivity of the water vapor will be measured and correlated to infrared absorption by measuring recirculating moist air in the cabinets shown in Figures 12 and 13.

Close interrelationships which were not previously understood exist between this work and that of investigators in cloud physics, electrical and electrostatic phenomena, and electromagnetic propagation of the atmosphere. Provocative evidence exists that since the extent of clustering and spectral absorption is proportional to the ionization level in water vapor, the phenomenon may become progressively more important with altitude because of cosmic radiations. Since the great majority of the earth's radiative transfer takes place in the 8-13 μ m infrared "window" wavelength region, whose opacity is greatly affected by the continuum absorption attributed to ion-induced clusters, the cluster mechanisms may have important effects upon global weather and climate.

A thermal blanket of continuum absorption should result in the presence of intense ionizing radiation or energy in other forms. Thus, nuclear blasts might directly affect radiative transfer and infrared systems operation in an ionized atmosphere. In normal atmospheric conditions, the opacity of the natural absorption blanket would vary directly as the square of changes in saturation ratio, and linearly with temperature.

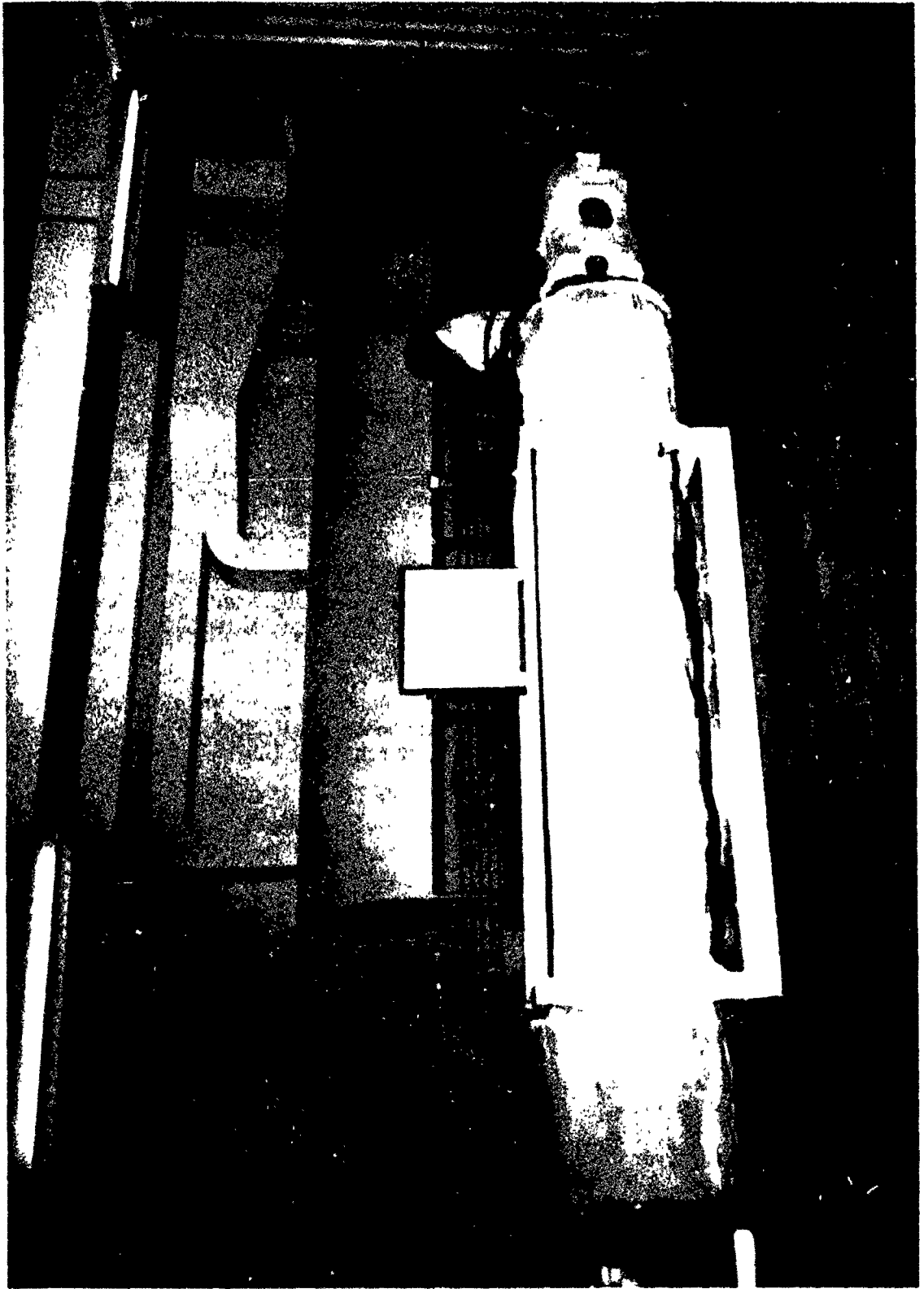


Figure 16. Multi-Pass Optical Cell Providing Paths up to 200 Meters

References:

1. R.E. Roberts, J.E.A. Selby and L.M. Biberman, "Infrared Continuum Absorption by Atmospheric Water Vapor in the 8.12um Window", Applied Optics 15, 2085 (1976).
2. H.R. Carlon, "Phase Transition Changes in the Molecular Absorption Coefficient of Water in the Infrared: Evidence for Clusters", Applied Optics 17, 3192 (1978).
3. H.R. Carlon, "Molecular Interpretation of the IR Water Vapor Continuum: Comments", Applied Optics 17, 3193 (1978).
4. H.R. Carlon, "Variations in Emission Spectra from Warm Water Fogs: Evidence for Clusters in the Vapor Phase", Infrared Physics 19, 49 (1979).
5. H.R. Carlon, "Ion Content and Infrared Absorption of Moist Atmospheres", J. Atmospheric Sciences (May, 1979).
6. H.R. Carlon, "Do Clusters Contribute to the Infrared Absorption Spectrum of Water Vapor?", accepted for publication in Infrared Physics (1979).
7. H.R. Carlon, "Introduction to Polymolecular Water Clusters and Their Infrared Activity", Chemical Systems Laboratory Technical Report ARCSL-TR-78014, Aberdeen Proving Ground, MD 21010, February 1978 (AD A052 699).
8. H.R. Carlon, "Final Report: Infrared Absorption by Water Clusters", Chemical Systems Laboratory Technical Report ARCSL-TR-79013, Aberdeen Proving Ground, MD 21010, March 1979 (AD number to be assigned).
9. F. Franks, ed., "Water: A Comprehensive Treatise", Vol. 1, The Physics and Physical Chemistry of Water; Plenum Press, New York, New York. pp. 502-504. 1972.
10. H. Israel, "Atmospheric Electricity", Vol. 1, Israel Program for Scientific Translations at Jerusalem (1971).
11. A.W. Castleran, Jr., and I.N. Tang, "Role of Small Clusters in Nucleation About Ions", J. Chem. Phys. 57, 3629 (1972).
12. J.A. Chalmers, "Atmospheric Electricity", Pergamon Press, pp. 86-88 (1967).
13. H. Gerdien, Phys. Z. 6, 800 (1905).
14. H.L. Wright, Proc. Phys. Soc. London 48, 675 (1936).
15. D.C. Blanchard, "The Electrification of the Atmosphere by Particles from Bubbles in the Sea", Woods Hole Oceanographic Institute, Reference 61-9.
16. A.D. Moore, ed., "Electrostatics and its Applications", New York, Wiley & Sons, p. 390 (1973).

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